

# CATALYZED CARBON GASIFICATION: THERMAL DESORPTION STUDIES ON CARBON-OXYGEN SURFACE COMPLEXES

Ramkrishna V. Nayak and Robert G. Jenkins

Fuel Science Program  
Department of Materials Science and Engineering  
The Pennsylvania State University, University Park, PA 16802

## INTRODUCTION

The exposure of a clean carbon surface to oxygen results in the formation of stable oxygen complexes (1). A large variety of studies, e.g., chemisorption, desorption, and spectroscopic, have been performed to understand the nature, composition and stability of these complexes (2-12). The programmed temperature desorption techniques have proved to be useful in yielding information on the total amount of oxygen present on the carbon surface, the amounts of CO and CO<sub>2</sub> in the desorbed product and the energetics of the complex desorption. Many workers have used temperature programmed desorption techniques to study the carbon-oxygen surface complexes (10-12). However, the majority of the work has been performed on "pure" carbons. Very little work has been conducted previously on the effect of added catalyst(s) on the decomposition of carbon-oxygen surface complexes. In recent studies on a graphitized furnace black, Vulcan 3 (V3G), it has been found that deposition of Pt on the carbon surface leads to significant enhancement of the C-O<sub>2</sub> reaction rate (13). To elucidate the cause of this enhanced reactivity it was decided to conduct linear temperature programmed desorption (LTPD) studies of the carbon-oxygen surface complexes formed on the Pt-V3G.

## EXPERIMENTAL

i. Materials - A graphitized furnace black, Vulcan 3, was used in this investigation. The graphitization procedure used is described elsewhere (15). The V3G has a total surface area (BET, N<sub>2</sub>, 77 K) of about 60 m<sup>2</sup>/g (16). Platinum was deposited on the V3G from a chloroplatinic acid solution. Subsequently, chloroplatinic acid was reduced to Pt by heating the sample to 775 K in flowing H<sub>2</sub> for 15 h. Two samples of V3G with differing amounts of Pt were prepared. The Pt content in the two samples was 0.075% and 1.07% (wt), respectively. These samples are referred as 0.075% Pt-V3G and 1.07% Pt-V3G.

ii. Apparatus - The LTPD studies were conducted in a horizontal mullite tube furnace. Samples (~1-1.2 g) were held in an alumina boat. The furnace temperature was controlled using a Eurotherm analog temperature controller and programmer unit. The sample temperature was measured about 5 mm above the center of the boat using a chromel-alumel thermocouple. Concentrations of CO and CO<sub>2</sub> in the N<sub>2</sub> stream during desorption were measured continuously using nondispersive infrared analyzers (Beckman Model 865). In this system the sensitivity to measure CO and CO<sub>2</sub> in the gas stream was approximately 1 ppm and 0.5 ppm, respectively. Gas flow rates were controlled using fine needle valves and measured using a soap-bubble meter. Oxygen chemisorption was performed using dry grade air. Desorption was performed in flowing ultra high purity nitrogen (99.999%).

iii. Procedure - In the case of 0.075% Pt-V3G and 1.07% Pt-V3G samples, the procedure involved first burning off the sample to 24% weight loss in air at a selected temperature. Subsequently, LTPD was performed. Later a series of oxygen chemisorption-LTPD experiments were carried out on the same sample in-situ. Desorption was always carried out in flowing nitrogen (300 cc/min) at 5 K/min heating rate to the maximum temperature of 1230 K and 3 h soak time. Thus, the sequence for a Pt-V3G sample was (a) initial reaction (B.O.), (b) desorption,

(c) oxygen adsorption, (d) desorption, (e) oxygen adsorption, (f) desorption. In the case of pure V3G, the sample used already had been gasified to 24% burn-off (B.O.) in a separate tube furnace at 723 K in 0.1 MPa of dry air. Therefore, in the case of pure V3G sample the sequence was somewhat different. The gasification reaction temperature selected for the 3 samples (pure V3G, 0.075% Pt-V3G and 1.07% Pt-V3G) were different such that the reaction rate for the three samples would be similar during the gasification. All the three samples were burned-off to the same level of activation (24%). The additional gasification that occurred during adsorption-desorption cycles was small (~1%) and was neglected.

## RESULTS AND DISCUSSION

Data obtained in each run consist of CO and CO<sub>2</sub> desorption rates as a function of temperature/time. Figure 1 and Figure 2 show the desorption profiles of CO and CO<sub>2</sub>, respectively, obtained for the 3 samples under the same chemisorption conditions. These figures do not show the desorption rates during the 3 h soak period. The desorption profiles obtained under the different chemisorption conditions were similar in overall nature. The CO desorption rate in all cases did not stop at 1230 K, but upon soaking the sample for 3 h at 1230 K, the desorption rates reduced to a very low level. As can be seen, the CO and CO<sub>2</sub> desorption rate profiles are very different. As examples, CO<sub>2</sub> desorption started at a lower temperature than did the CO desorption; the evolution of CO<sub>2</sub> was complete in a temperature range where the CO desorption rate was reaching a peak; and the CO<sub>2</sub> desorption profiles had more peaks than did the CO profile. In these experiments it was always found that the amount of oxygen complex that desorbed as CO<sub>2</sub> was much less than that desorbed as CO (see Table I). From the studies performed at different temperatures it was found that as the chemisorption temperature was lowered (713-303 K) then the temperature at which the CO desorption started was also lowered. However, the temperature at which the CO desorption rate was a maximum seemed to be independent of the chemisorption temperature (and, thereby, also was independent of the amount of oxygen on the surface). This suggests that the CO desorption rate is a unimolecular process (17). In all cases, a shoulder in the CO desorption rate appeared at high temperature (1100-1230 K). The presence of a shoulder indicates the presence of more than one kind of sites and/or oxygen complexes desorbing as CO. As was the case for CO desorption, the CO<sub>2</sub> desorption started at lower temperature if the O<sub>2</sub> chemisorption was performed at lower temperature. The temperatures at which peaks in CO<sub>2</sub> evolution rate appeared also seemed to be independent of the chemisorption temperature (and, thus, of the amount of O<sub>2</sub> on the surface). Again, this suggests first order decomposition behavior for CO<sub>2</sub>. Presence of Pt appears to have shifted the peak in CO desorption rate to a slightly lower temperature (965 K to 950 K). However, the higher temperature shoulder appears to be little affected by the presence of Pt. It should be noted that desorption of CO<sub>2</sub> appears to be markedly accelerated by Pt. For Pt containing samples the low temperature peak (570 K) was present. However, this peak was absent in the pure V3G desorption profile. Also, proportionately more CO<sub>2</sub> desorbed at lower temperatures in the case of Pt-V3G compared to pure V3G.

The desorption profiles can be integrated to obtain total amount of oxygen desorbed as CO and CO<sub>2</sub> in each case. Table I gives the total amount of oxygen and the amount of oxygen that desorbed as CO and CO<sub>2</sub> from the 3 samples. The amount of oxygen chemisorbed increased with increasing chemisorption temperature. It also increased with increase in Pt content. The amount of O<sub>2</sub> associated with Pt in these cases was very small (~5%) and was neglected.

The amount of oxygen chemisorbed on a carbon sample can be used to determine the active surface area of the carbon as described by Laine et al. (19). In the case of 0.075% Pt-V3G (24% B.O.), the amount of oxygen chemisorbed at 473 K and 0.1 MPa air for 12 h corresponded to about 10% of the total surface area. For 1.07% Pt-V3G (23.5% B.O.) and V3G (24% B.O.) the amount of O<sub>2</sub> chemisorbed at 473 K

and 0.1 MPa air corresponded to about 13% and 6.5% of the total surface area, respectively. This significantly higher amount of oxygen adsorbed in the presence of Pt could be due to spillover of  $O_2$  from Pt onto carbon basal planes.

The desorption rate versus temperature data can also be treated mathematically to yield surface complex/site energy distribution as a function of surface coverage (14). Figure 3 and Figure 4 show for CO and  $CO_2$ , respectively, the desorption surface site/complex energy ( $E_d$ ) as a function of surface coverage. For both gases, as the surface was uncovered the activation energy for desorption increased. The variation in  $E_d$  for CO desorption (Figure 3) with surface coverage was essentially linear for most of the surface coverage (0.2-0.8) whereas at the beginning and the end of the surface coverage, the variation in  $E_d$  was marked. The  $CO_2$  desorption energy varied in a linear fashion for the intermediate surface coverage. But for small surface coverage (<0.2) and large surface coverage (>0.8),  $E_d$  varied rather rapidly. The activation energy for  $CO_2$  desorption varied between 112 KJ/mole to 300 KJ/mole and for CO, the activation energy varied between 200 KJ/mole to 400 KJ/mole. These values agree well with the values listed in the literature (12,14,22).

Figures 3 and 4 also show the variation in  $E_d$  for CO and  $CO_2$  as a function of surface oxygen coverage for the 3 different samples, V3G (24% B.O.), 0.075% Pt-V3G (24% B.O.), 1.07% Pt-V3G (23.5% B.O.). Chemisorption on these samples was done under the same conditions of temperature and pressure (473 K, 0.1 MPa air). For the CO desorption energy, the effect of Pt appears to be small. The  $CO_2$  desorption energy as a function of surface coverage shows marked difference as Pt content on V3G increases. The activation energy for the surface complex desorption of  $CO_2$  decreased, at the same surface coverage, with increase in Pt content. In other words, the presence of Pt appears to help in desorption of  $CO_2$  complexes. This agrees with the reactivity measurements performed on these samples using a TGA and a flow reactor with nondispersive infrared detectors (13). In the case of Pt-V3G,  $CO_2$  was found to be the sole gasification product at 723 K (0.1 MPa air). The reactivity of 1.07% Pt-V3G was about 400 times higher compared to that of pure V3G. As Pt content increased the sample reactivity increased. This increase in measured reactivity with Pt content is probably related to the ease of decomposition of oxygen complexes as  $CO_2$  because no CO was detected in the gasification step.

#### CONCLUSION

The surface of V3G is heterogeneous in nature and several types of surface oxygen species are formed upon its exposure to  $O_2$ . With addition of Pt, the amount of  $O_2$  chemisorbed on V3G increases. Under the conditions used in this study, a significant portion of the V3G total surface was covered with oxygen, indicating, probably, spillover of oxygen from Pt onto the carbon surface. The stability of the surface oxygen complexes depends upon the conditions of temperature and pressure under which they are formed. The presence of Pt on the V3G further changes the stability of the surface oxygen complexes. LTPD is a very useful technique to study the stabilities of the surface oxygen species formed on a carbon surface. Using this technique it is found that the presence of Pt affects the stability of both CO and  $CO_2$  forming surface oxygen species. But the effect on the  $CO_2$  forming surface oxygen species is much more than the CO forming surface species. This results in a decrease in activation energy for  $CO_2$  desorption at the same fractional surface coverage from Pt-V3G compared to pure V3G. The reactivity measurements performed on these samples showed that Pt enhances the reactivity of V3G in  $O_2$  by at least 2 orders of magnitude and  $CO_2$  is the sole reaction product upto 775 K.

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Table 1: Oxygen Chemisorption Conditions and Desorption Product Composition

Run #	Sample Type	Adsorption Condition	Desorption Products			Total O <sub>2</sub> Desorbed ( $\mu$ mole/g)
			CO ( $\mu$ mole/g)	CO <sub>2</sub> ( $\mu$ mole/g)	Ratio (CO/CO <sub>2</sub> )	
1	0.075% Pt-V3G	758 K-0.1 MPa Air-24 h (in-situ B.O. to 24%)	305.0	15.0	20.3	167.5
2	0.075% Pt-V3G (24% B.O.)	473 K-0.1 MPa Air-12 h	154.0	18.5	8.3	95.5
3	0.075% Pt-V3G (24% B.O.)	303 K-0.1 MPa Air-16 h	53.0	7.8	6.8	34.3
4	1.07% Pt-V3G	713 K-0.1 MPa Air-24 h (in-situ B.O. to 23.5%)	388.5	30.1	12.9	224.4
5	1.07% Pt-V3G (23.5% B.O.)	473 K-0.1 MPa Air-12 h	186.5	27.0	6.9	120.2
6	1.07% Pt-V3G (23.5% B.O.)	303 K-0.1 MPa Air-16 h	97.0	15.0	6.5	53.5
7	V3G (24% B.O.)	823 K-0.1 MPa Air-1 h	176.5	6.9	25.6	95.2
8	V3G (24% B.O.)	473 K-0.1 MPa Air-12 h	64.0	8.5	7.6	40.5

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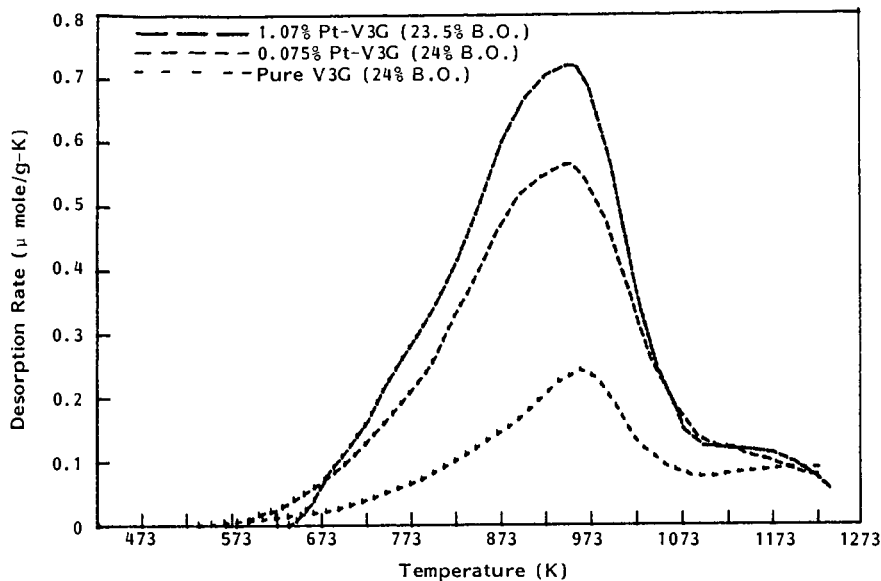


Figure 1: CO Desorption Profiles After 473 K-12 h Chemisorption

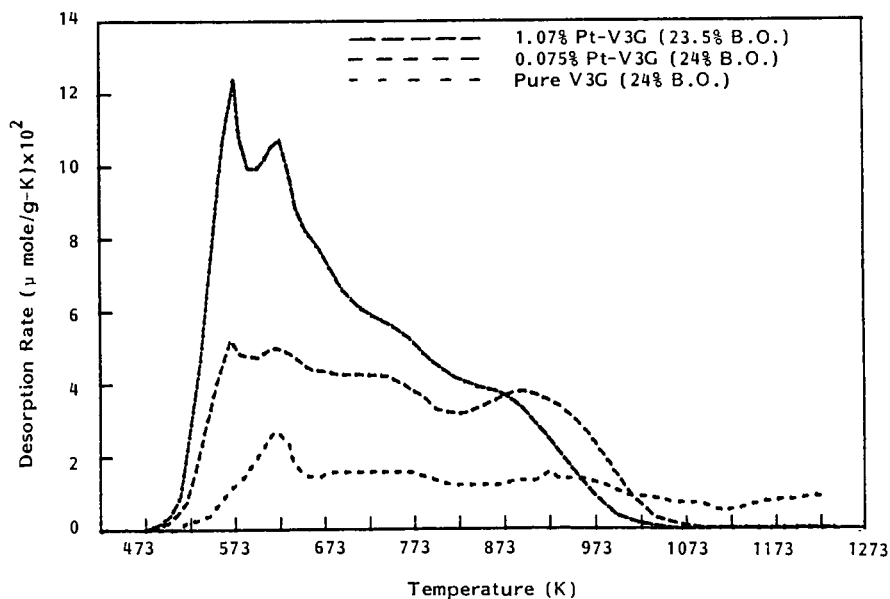


Figure 2: CO<sub>2</sub> Desorption Profiles After 473 K-12 h Chemisorption

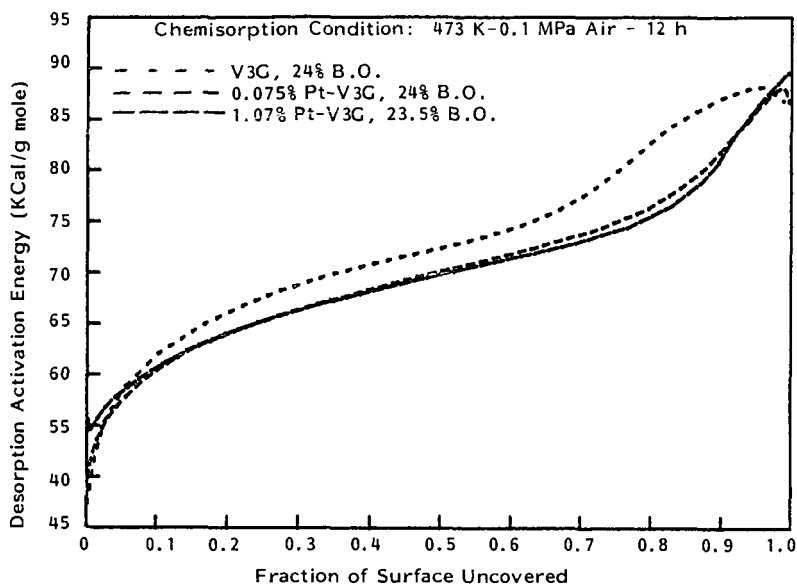


Figure 3: Surface Energy Distribution Profiles Obtained from CO Desorption Profiles

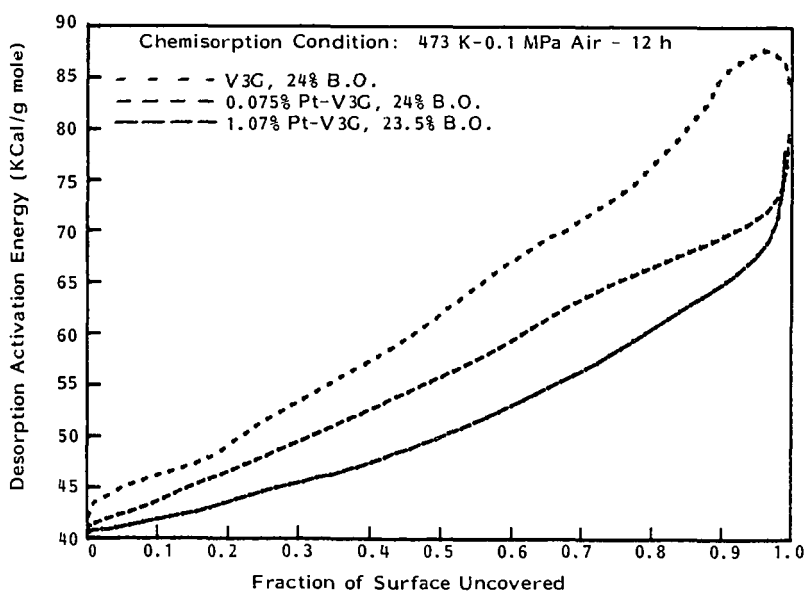


Figure 4: Surface Energy Distribution Profiles Obtained from CO<sub>2</sub> Desorption Profiles